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13. ABSTRACT (Maximum 200 words) Polyelectrolytes, where anions are covalently bonded to the backbone have unit transference number for cations and are therefore, attractive for high energy density batteries. In this project, we prepared new polyelectrolyte materials and modeled the behavior of polyelectrolytes, to understand differences between polyelectrolyte conduction and polymer/salt complex electrolyte conduction. Major results include: 1. Reduction of the basicity of the anion in a polyelectrolyte by the development of aluminosilicate polyelectrolyte materials. 2. Development of nanocomposite polyelectrolytes, consisting of a polymer intercalated into clay materials. Demonstration that conduction in these materials is limited both by tortuosity effects and by the inherent mobility of the ion in the polymer. 3. Modeling demonstrates clearly that polyelectrolyte conduction will be reduced compared to polymer/salt complex electrolyte production, both because of the lack of anion mobility and because of higher average barriers due to rigidity of the polyanionic structure. We suggested a number of structural modifications that are likely to increase polyelectrolyte conduction.					
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DESIGN, SYNTHESIS AND THEORY OF ION TRANSPORT
IN A NEW CLASS OF SOLID POLYELECTROLYTES

FINAL PROGRESS REPORT

FOR PERIOD COVERING

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A. Statement of the Problem Studied

The two goals of this research were to prepare improved polyelectrolyte materials for cation conduction in secondary batteries, and to model the mechanistic bottlenecks to increased conduction, that limit power density in the final batteries.

Solutions of these two problems is crucial if advanced batteries based on polyelectrolytes are to be developed. Such batteries would have both high energy density and high power density, in addition to the other advantages of polymer-based batteries (stability, low cost, light weight, dimensional variability, safety, environmental compatibility).

B. Summary of Most Important Results

We feel that this research project has been extremely successful. Major accomplishments include:

1. Synthesis of new, single-phase polyelectrolyte materials based on reduced basicity an ionic centers. For example, in aluminosilicate structures, the effective basicity of the aluminate center can be reduced by inserting a silicon in place of a carbon beyond the first oxygen site. This reduced basicity results in less effective ion pairing, and therefore in higher cationic mobility and conductivity.
2. Preparation of composite polyelectrolyte materials, consisting of alkaline montmorillonite clays filled with a polymer such as polyphosphazene. These materials exhibit unit transference number for cations, dimensional and structural stability, and relatively high conduction. This conduction is limited both by the inherent mobility of the ion in the polymer, and by tortuosity effects due to particle size of the clays. Reduction of clay particle sizes reduces the tortuosity impediment and results in higher bulk reduction.

3. Demonstration of the effect of added complexing agents such as cryptands in increasing polyelectrolyte conduction, due to reduction of ion clustering and pairing.
4. Demonstration that increased dielectric constant of the polymer can indeed increase ionic conductivity, but that the fluidity of the polymer remains the dominant factor. Polycarbonates, therefore, are not a productive pathway, because their relatively high electric constant is more than balanced by their higher glass transition temperatures.
5. Demonstration based on mechanistic modeling that polyelectrolyte conduction will generally be lower than polymer/salt complex conduction, although the unity transference number for cations provides a substantial practical advantage in reducing salt polarization. Conduction drop in polyelectrolytes is due both to the lack of contribution from anions, and to the increased cation trapping, due to fixed, rather than mobile, counter-charge. Suggestions for structures to enhance polyelectrolyte conduction, both by reduced basicity and by increased flexibility of the anion tether, follow from these simulations.

The attached two figures are demonstrative of the findings of this research. Figure 1 shows a cartoon of the structure of a montmorillonite clay/sodium polyphosphazene composite electrolyte. In this case, the clay particles are flake-like in geometry, so that there is a tortuosity penalty for conduction perpendicular to the film, as opposed to parallel to the film. The activation energy for conduction shows clearly that the temperature dependence is dominated in both cases by the same factors (the slopes are the same), arising from the inherent mobility of the ion in the polymer host. The prefactors differ because of tortuosity.

Figure 2 shows the results of dynamic percolation studies of polyelectrolyte

materials, compared to analogous polymer/salt complex materials. The reduced conduction arises, as stated above, both from trapping of the cation and from the missing anion contribution. The effects that facilitate conduction in complex materials (lower glass transition temperature, reduced ion pairing) also increase cation conduction in polyelectrolytes.

Based on these observations, we believe that there are a number of very promising avenues for improved polyelectrolytes: these avenues will include flexible polyelectrolyte structures to reduce cation trapping, composite polyelectrolyte structures to increase interfacial conduction and provide a conductivity increment from polarization effects, and further reduction in local basicity arising from controlled structures in the polyelectrolyte. These are topics for future research in our laboratory.

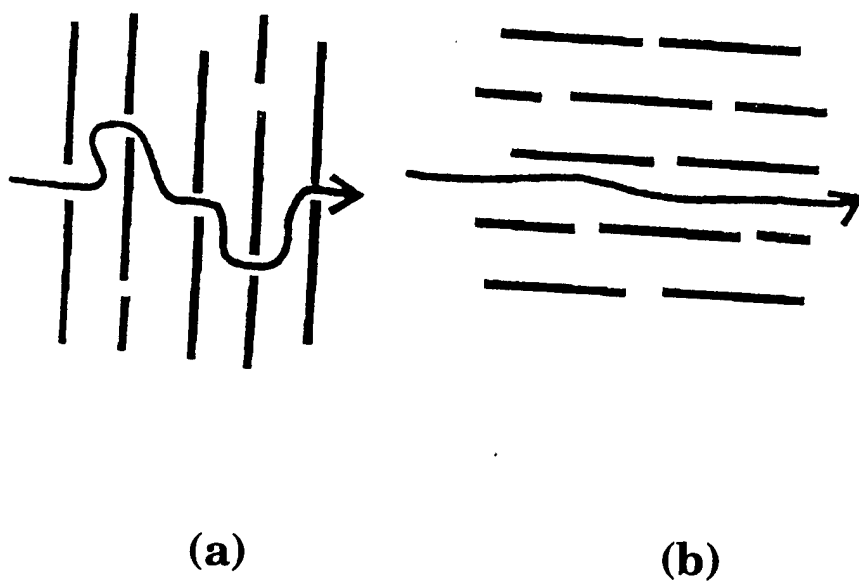


Figure 1: Schematic illustration of ion transport (a) perpendicular and (b) parallel to montmorillonite layers in montmorillonite polymer composites.

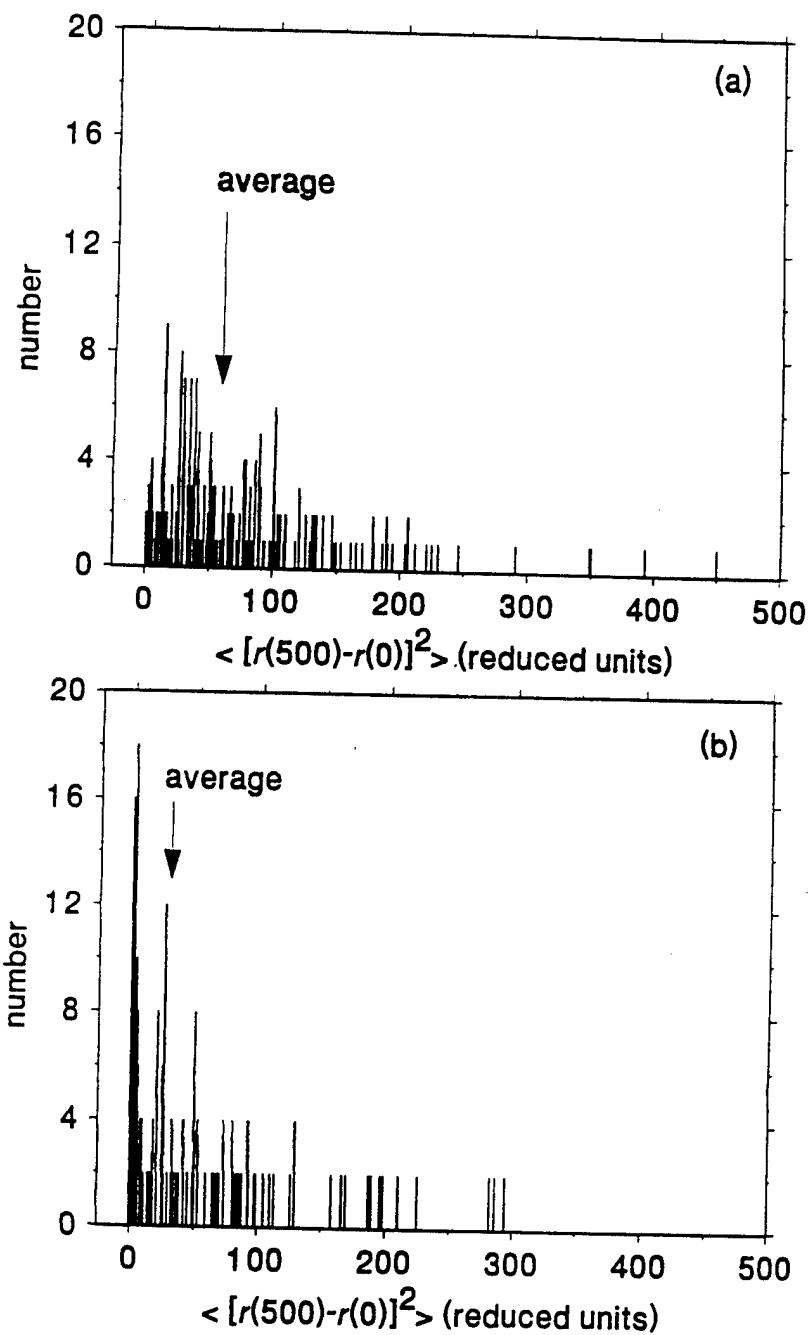


Figure 2: Dynamic percolation of (a) polymer salt complex
(b) polyelectrolyte

C. Publications

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